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Kinetics of absorption of carbon dioxide in aqueous piperazine solutions

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Abstract

In the present work the absorption of carbon dioxide into aqueous piperazine (PZ) solutions has been studied in a stirred cell, at low to moderate temperatures, piperazine concentrations ranging from 0.6 to 1.5 kmol m^{-3}, and carbon dioxide pressures up to 500 mbar, respectively. The obtained experimental results were interpreted using the DeCoursey equation [DeCoursey, W., 1974. Absorption with chemical reaction: development of a new relation for the Danckwerts model. Chemical Engineering Science 29, 1867–1872] to extract the kinetics of the main reaction, $2PZ + CO_2 \rightarrow PZCOO^- + PZH^+$, which was assumed to be first order in both CO_2 and PZ. The second-order kinetic rate constant was found to be 70 $m^3\,mol^{-1}\,s^{-1}$ at a temperature of 298.15 K, with an activation temperature of 4.1×10^3 K. Also, the absorption rate of CO_2 into partially protonated piperazine solutions was experimentally investigated to identify the kinetics of the reaction $2PZH^+ + CO_2 \rightarrow H^+PZCOO^- + PZH_2^{2+}$. The results were interpreted using the Hogendoorn approach [Hogendoorn, J., Vas Bhat, R., Kuipers, J., Van Swaaij, W., Versteeg, G., 1997. Approximation for the enhancement factor applicable to reversible reactions of finite rate in chemically loaded solutions. Chemical Engineering Science 52, 4547–4559], which uses the explicit DeCoursey equation with an infinite enhancement factor which is corrected for reversibility. Also, this reaction was assumed to be first order in both reactants and the second-order rate constant for this reaction was found to be (0.28 ± 0.10) $m^3\,mol^{-1}\,s^{-1}$ at 298.15 K.

Keywords: Carbon dioxide; Piperazine; Absorption; Kinetics; Mass transfer

1. Introduction

Reactive absorption of acid gas components (such as CO_2 and H_2S) from industrial and natural gas streams has been an important part in many industrial processes for decades. The solvents used in these gas treating processes are usually aqueous solutions of alkanolamines (Kohl and Nielsen, 1997). For particular applications, however, also combinations of solvents are used (e.g. the shell sulfolane process). The suitability of an alkanolamine for a certain process is—among others— determined by the characteristics of its kinetics with CO_2. Since the reaction of all alkanolamines with H_2S only involves a proton transfer, its rate can be considered as instantaneous with respect to mass transfer, and thus detailed knowledge of the reaction kinetics of H_2S is of no importance. Recent interest and developments in the bulk removal of CO_2, owing to the Kyoto agreement, involve the addition of an activator (usually a primary or secondary amine) to an aqueous *N*-methyldiethanolamine (MDEA) solution. The reason for the use of such a blend is related to the relatively high rate of reaction of CO_2 with the activator combined with the advantages of MDEA concerning regeneration and stoichiometric loading capacity, which leads to higher rates of absorption in the absorber column while maintaining a low heat of regeneration in the stripper section.

The use of piperazine ($C_4H_{10}N_2$) activated aqueous MDEA solutions was patented by BASF as it proved to be successful when applied in the bulk removal of CO_2 in ammonia plants (Appl et al., 1982). Since then, several studies have reported on the characteristics and performance of piperazine activated blends:

- PZ activated aqueous MDEA solutions (Bishnoi and Rochelle, 2002a,b; Liu et al., 1999; Xu et al., 1992, 1998; Zhang et al., 2001, 2003);

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- PZ activated aqueous AMP solutions (Seo and Hong, 2000; Sun et al., 2005);
- PZ activated aqueous MEA solutions (Dang and Rochelle, 2003);
- PZ activated aqueous K_2CO_3 solutions (Cullinane and Rochelle, 2004, 2005).

Whereas published research on the application of all of the (bulk) amines (such as MDEA, AMP and MEA) is extensive—see e.g. the literature survey on the kinetics between CO_2 and various alkanolamines by Versteeg et al. (1996)—there are only few studies dealing with single aqueous piperazine solutions. Carbon dioxide solubility data have been reported by Aroua and Mohd Salleh (2004), Bishnoi and Rochelle (2000), Derks et al. (2005a) and Pérez-Salado Kamps et al. (2003), but only two studies on the absorption rate of CO_2 into aqueous piperazine solutions—that can be used to extract kinetic rate data—have been published in literature (Bishnoi and Rochelle, 2000; Sun et al., 2005). This might seem logical due to the fact that, in industry, piperazine is only used in combination with other (alkanol)amines rather than as a stand-alone solvent, but information on the kinetics of the individual components of a solvent with CO_2 is essential for a better understanding of the mechanism and working principle of the absorption process of CO_2 in blends of alkanolamine solutions. Moreover, in rigorous flux models all these reaction kinetics are required input parameters (Versteeg and Van Swaaij, 1988a). Once experimentally observed fluxes of CO_2 into aqueous piperazine solutions can be understood and simulated accurately, it is possible to theoretically predict the behaviour of blends of piperazine with other (alkanol)amines.

Therefore, the present work will focus on the experimental absorption of CO_2 into aqueous piperazine solutions, at low to moderate temperatures, different piperazine concentrations and CO_2 partial pressures to obtain more insights into the kinetics of CO_2 with piperazine. Absorption data obtained in the so-called pseudo first-order reaction regime (Danckwerts, 1979) will be used to determine the kinetics of the reaction between CO_2 and PZ in aqueous solution.

2. Kinetics

In aqueous environment, piperazine can react with CO_2 to form many different reaction products, as shown by Bishnoi and Rochelle (2000) and Ermatchkov et al. (2002). In aqueous piperazine solutions, carbon dioxide can react according to reactions (1)–(5):

- reaction (1), R1:

$$CO_2 + PZ + B \rightleftarrows PZCOO^- + BH^+,$$

- reaction (2), R2:

$$CO_2 + PZCOO^- + B \rightleftarrows PZ(COO^-)_2 + BH^+,$$

- reaction (3), R3:

$$CO_2 + PZH^+ + B \rightleftarrows H^+PZCOO^- + BH^+,$$

Table 1
Reactants and their pK_a values

Reaction	Reactant	pK_a ($T = 25\,^\circ C$)	Source
R1	PZ	9.731	Hetzer et al. (1967)
R2	$PZCOO^-$	9.44	Ermatchkov et al. (2002)[a]
R3	PZH^+	5.333	Hetzer et al. (1967)

[a]Calculated from equilibrium constant.

- reaction (4), R4:

$$CO_2 + OH^- \rightleftarrows HCO_3^-,$$

- reaction (5), R5:

$$CO_2 + H_2O \rightleftarrows H_2CO_3,$$

where B is any base present in solution (PZ, $PZCOO^-$, PZH^+, H_2O and OH^-).

The aim of this work is to identify the most important reaction(s) and the corresponding mechanism(s) and kinetic constant(s). Based on the previous studies by Bishnoi and Rochelle (2000) and Sun et al. (2005), reaction (1) is expected to be the major contributor to the overall observed absorption rate. However, in order to come to the correct kinetic rate (constant) of this reaction, it is important to qualitatively and/or quantitatively determine the (relative) contributions of the other reactions.

The contribution of reaction (5) to the overall rate of absorption into an amine solution can easily be neglected based on the equilibrium constant of this reaction in comparison to the other reactions (see e.g. the piperazine–CO_2 equilibrium studies, Bishnoi and Rochelle, 2000; Derks et al., 2005a; Pérez-Salado Kamps et al., 2003, mentioned in Section 1). Also, the relative contribution of reaction (4) is assumed to be negligible to the overall absorption rate: both the forward rate constant (as e.g. determined by Pohorecki and Moniuk, 1988) and the hydroxide ion concentration in the solution (which can be estimated from the pK_a of piperazine and the water hydrolysis equilibrium constant) are much smaller than both the concentration of piperazine and the published values for the kinetic rate constant of reaction (1), respectively—as shown by Sun et al. (2005).

Forward rate constants of reactions (2) and (3) are not available in the literature, but a first estimation for these rate constants can be made using the Brønsted dependency of the reactivity on the pK_a (Penny and Ritter, 1983): this technique has shown that for many alkanolamines, a (linear) relation between the pK_a value of an (alkanol)amine and (the logarithm of) the forward rate constant exists. Table 1 lists the pK_a values as found in the literature for the reactants of reactions (1)–(3).

If it is assumed that this Brønsted relation is also applicable to piperazine, it seems reasonable to disregard reaction (3), since its forward kinetic rate constant is expected to be a few orders of magnitude smaller than the rate constant for reaction (1), considering the difference in pK_a between PZ and PZH^+. The validity of this assumption will be checked experimentally later on.

Assuming the above mentioned Brønsted relation dependence, reaction (2) cannot be neglected beforehand on the basis of a lower pK_a with respect to reaction (1), since the difference is marginal. At this point, it is therefore not possible to exactly determine the effect of this reaction on the overall absorption rate. A worst case estimation, however, can be made. Suppose that the forward kinetic rate constants of reactions (1) and (2) are identical in order of magnitude. This seems a reasonable, optimistic estimate comparing their pK_a values. In that case, the relative contributions of these reactions are determined by the concentrations of the main reactants PZ and $PZCOO^-$. Kinetic experiments are preferably, also in this study, carried out in the so-called pseudo-first-order regime (see Section 3). In this regime, the (interfacial) concentration of (in this case) piperazine is not noticeably decreased due to the reaction with CO_2, and hence the concentration of the reaction product—carbamated piperazine—will be small compared to the remaining piperazine concentration (even close to the gas–liquid interface) and, consequently, the carbamated piperazine can only make a small contribution to the overall absorption rate via reaction (2).

Based on all considerations concerning the various reactions with carbon dioxide in aqueous solutions of piperazine, it seems justified to conclude that the overall absorption rate is, in the kinetic regime where the enhancement factor equals the *Ha* number, solely influenced by reaction (1), and therefore determination of the kinetics of reaction (1) will be the main result of the experimental part of this work. Also, as noted above, the hypothesis on the rate of reaction (3) is experimentally validated in this study.

2.1. Reaction mechanism

The kinetics of primary and secondary alkanolamines with CO_2 can be described using the zwitterion mechanism, as originally proposed by Caplow (1968) and later reintroduced by Danckwerts (1979). It is assumed that this mechanism is also applicable to PZ although it is not an alkanolamine: piperazine will react with CO_2, the rate being first order both in CO_2 and PZ, respectively, under the formation of a zwitterion, which is consequently deprotonated by any base B present in the liquid, also according to an overall second-order (first with respect to PZH^+COO^- and B) reaction rate:

$$PZ + CO_2 \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} PZH^+COO^-, \tag{1}$$

$$PZH^+COO^- + B \overset{k_B}{\rightleftarrows} PZCOO^- + BH^+. \tag{2}$$

Assuming a quasi-steady-state condition for the zwitterion concentration and an irreversible deprotonation step, the kinetic rate equation is given by

$$R_{CO_2} = \frac{k_2[PZ][CO_2]}{1 + k_{-1}/\sum k_B B} = \frac{[PZ][CO_2]}{1/k_2 + (k_{-1}/k_2)(1/\sum k_B B)}, \tag{3}$$

where $\sum k_B B$ is the contribution of all the bases present in the solution (PZ, $PZCOO^-$, PZH^+, H_2O and OH^-) for the removal of the protons. As e.g. Kumar et al. (2003) pointed out, there are two asymptotic situations for amines in aqueous solution:

(I) In case the deprotonation of the zwitterion is very fast, or $k_{-1}/\sum k_B B \ll 1$, the kinetic equation reduces to simple second-order kinetics, as found for primary alkanolamines such as MEA:

$$R_{CO_2} = k_2[CO_2][PZ]. \tag{4}$$

(II) The reversed situation of case I occurs when $k_{-1}/\sum k_B B \gg 1$. Now the kinetic rate expression reduces to 5.

$$R_{CO_2} = k_2[PZ][CO_2]\left(\frac{\sum k_B B}{k_{-1}}\right). \tag{5}$$

Now the reaction order is dependent on the contribution of the individual bases to the deprotonation of the zwitterion. This expression can also account for a shift in reaction order with changing amine concentration, as typically found in the kinetic rate expression of many secondary alkanolamines with CO_2 (Versteeg et al., 1996).

In the case of piperazine, both asymptotic options I and II seem plausible, since on one hand piperazine has a higher pK_a value than MEA, which—based on the Brønsted plot technique—results in a high deprotonation rate constant k_B and thus could point towards behaviour type I, whereas on the other hand both its amine groups are in fact secondary amines (like DEA) which would suggest a reactivity according to scenario II.

Both Bishnoi and Rochelle (2000) and Sun et al. (2005) concluded in their studies that aqueous piperazine reacts with CO_2 according to behaviour type I. Bishnoi and Rochelle (2000) drew this conclusion based on absorption rate experiments for piperazine concentrations of 0.2 and 0.6 kmol m^{-3} at approximately 298 K. Sun et al. (2005) based their conclusion on experiments conducted for a concentration range between 0.23 and 0.92 kmol m^{-3} at temperatures of 30, 35 and 40 °C.

The experimental focus of the present study will include CO_2 absorption rates into aqueous piperazine solutions at three different concentrations (up to 1.5 kmol m^{-3}). Experiments have been carried out at temperatures between 20 and 40 °C to investigate the temperature dependence of the reaction. Also, as already mentioned in the discussion on all occurring reactions, an attempt is made to quantify the reaction rate between CO_2 and the protonated piperazine species. Experimental methods and procedures are explained in Section 4.

3. Mass transfer

The absorption of a gas A into a reactive liquid is generally described by

$$J = \frac{(C_{A,G} - C_{A,L}/m)}{1/k_G + 1/mk_L E_A}. \tag{6}$$

Simplifications to Eq. (6) can easily be made, when assuming ideal gas behaviour and operating under the following (experimental) conditions:

a fresh and therefore lean liquid (and hence $C_{A,L} = 0$);
a pure gas.

Taking these considerations into account, the absorption of pure CO_2 is given by

$$J = k_L E_{CO_2} \frac{m P_{CO_2}}{RT}, \tag{7}$$

where the (chemical) enhancement factor E_{CO_2} is a function of the Hatta number Ha and the infinite enhancement factor E_{inf}.

The Hatta number is defined as

$$Ha = \frac{\sqrt{k_{ov} D_{CO_2}}}{k_L}, \tag{8}$$

where it is assumed that the total reaction rate k_{ov} is completely determined by reaction (1) as discussed in Section 2. Under the already mentioned additional assumption that the reaction is first order with respect to carbon dioxide (Section 2), this means

$$k_{ov} = \frac{R^1_{CO_2}}{[CO_2]}. \tag{9}$$

According to the penetration model (Higbie, 1935), the infinite enhancement factor, E_{inf}, is given by

$$E_{CO_2,\infty} = \sqrt{\frac{D_{CO_2}}{D_{Am}}} \left(1 + \frac{D_{Am}}{D_{CO_2}} \frac{[Am]RT}{\nu_{Am} P_{CO_2} m_{CO_2}}\right). \tag{10}$$

It must be noted, however, that Eq. (10) is only valid for irreversible reactions: for reversible reactions, the infinite enhancement factor decreases for lower values of the equilibrium constant, as shown in Appendix B. However, it will be shown later that the reversibility of the reaction does not play a significant role during the absorption experiments into aqueous piperazine solutions, so the use of Eq. (10) is justified.

Depending on the absolute value of Ha and the ratio between Ha and E_{inf}, three absorption regimes can be distinguished. For a constant value for the Hatta number ($Ha > 2$) and with decreasing infinite enhancement factor (for the experiments carried out at constant piperazine concentration this is related to an increasing CO_2 partial pressure), they are:

The pseudo-first-order regime: If the ratio between the Ha number and the infinite enhancement factor is sufficiently large, the following criterion will be obeyed:

$$2 < Ha \ll E_{inf}. \tag{11}$$

Upon satisfaction of Eq. (11), the reaction of CO_2 with the (alkanol)amine can be considered to take place in the pseudo-first-order regime and in that case the enhancement factor equals the Ha number. Consequently, Eq. (7) is changed to

$$J_{CO_2} = \sqrt{k_{ov} D_{CO_2}} \frac{m_{CO_2} P_{CO_2}}{RT}. \tag{12}$$

It is obvious from Eq. (12) that the experimentally observed absorption rate gives direct information on the kinetic rate constant k_{ov}.

The 'intermediate' regime: On increasing CO_2 partial pressures (and hence decreasing the value of the infinite enhancement factor), depletion of the amine at the interface starts to occur. In this 'intermediate' regime, it is not possible to derive the kinetic data directly from the CO_2 fluxes and the corresponding enhancement factors. For this 'intermediate' regime, an approximate solution for the enhancement factor as a function of both Ha and E_{inf} is derived by DeCoursey (1974):

$$E_{DC} = -\frac{Ha^2}{2(E_{inf}-1)} + \sqrt{\frac{Ha^4}{4(E_{inf}-1)^2} + \frac{E_{inf} Ha^2}{(E_{inf}-1)} + 1}. \tag{13}$$

Eq. (13) was derived for absorption with irreversible second-order (1,1) chemical reaction based on Danckwerts' surface renewal theory. Using the 'intermediate' regime to derive the kinetics of reversible reactions basically also requires knowledge about the equilibrium constant of the reaction as this constant influences E_{inf} (see Appendix B). Because of all these mutual interactions, this region is generally considered to be not attractive to derive the kinetics reliably.

The instantaneous regime: The third regime is reached when the infinite enhancement factor becomes significantly smaller than Ha, and now the following applies:

$$2 < E_{inf} \ll Ha. \tag{14}$$

Here, the reaction is said to be 'instantaneous' with respect to mass transfer, and the rate of absorption is completely limited by diffusion of the reactants and the determination of the kinetics from experimental absorption rate data is not possible. Here, the maximum possible enhancement factor applies and the flux for an irreversible reaction can be described as

$$J_{CO_2} = k_L \left(\sqrt{\frac{D_{CO_2}}{D_{Am}}} + \sqrt{\frac{D_{Am}}{D_{CO_2}}} \frac{[Am]RT}{\nu_{Am} m P_{CO_2}}\right) \frac{m P_{CO_2}}{RT}. \tag{15}$$

Since the kinetics of CO_2 with aqueous piperazine are not known in detail, it is not possible to determine beforehand in which regime absorption experiments are carried out. Therefore—at a constant temperature, liquid stirrer speed and piperazine concentration (and hence a constant Ha number)—a series of absorption experiments should be conducted, with decreasing CO_2 partial pressures, until a linear relationship is found between the experimental CO_2 flux and applied partial pressure—if the assumption concerning a first-order dependence of CO_2 in the kinetic expression is indeed correct. According to Eq. (12), kinetic rate data can then directly be extracted from the slope.

As mentioned, the reversibility of reaction (1) is not taken into account in the derivation of the mass transfer equations. In this study, it is assumed that the reaction can be regarded as irreversible due to the combination of a high value for the equilibrium constant (see Eq. (16) and Table 2) and the low

Table 2
Equilibrium constant values

Temp. [°C]	K_{Eq-1}[a] [m^{-1}]	pK_aPZ[b] (–)	K^{Eq} (m^{-1})
25	1.48×10^{-5}	9.731	8.0×10^4
40	9.40×10^{-6}	9.367	2.2×10^4

[a]Taken from Ermatchkov et al. (2002).
[b]Taken from Hetzer et al. (1967).

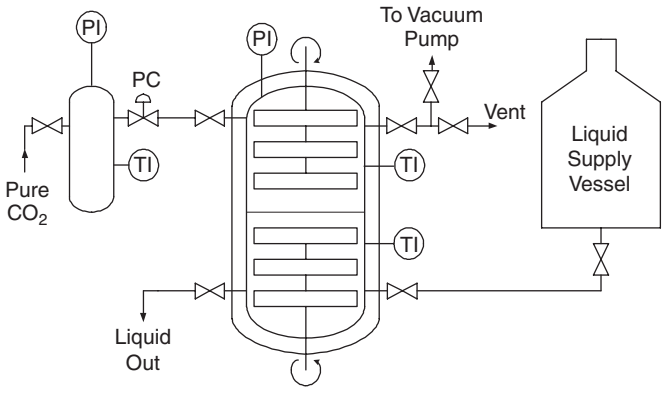

Fig. 1. Schematic diagram of the experimental set-up.

carbon dioxide loadings present during the experiments:

$$K_{eq} = \frac{[PZCOO^-][PZH^+]}{[CO_2][PZ]^2} = \frac{[PZCOO^-][H_3O^+]}{[CO_2][PZ][H_2O]} \cdot \frac{[PZH^+][H_2O]}{[H_3O^+][PZ]} = K_{Eq-1} \times 10^{pK_a,PZ}. \quad (16)$$

Even though the equilibrium constants listed in Table 2 are already fairly large, the influence of reversibility will be studied and discussed to verify the assumption regarding reaction (1) to be irreversible under the experimental conditions in the present work.

4. Experimental

The gas–liquid contactor used was a stirred cell reactor operated with a smooth and horizontal gas–liquid interface. The reactor consisted of glass, was thermostated and it was provided with magnetic stirrers in the gas and liquid phases, which could be controlled independently. Both the reactor and the gas supply vessel were equipped with PT-100 thermocouples and digital pressure transducers and measured signals were recorded in the computer. The pressure transducer connected to the stirred cell was a Druck DPI 260 (range 0–199.99 mbar) and the gas supply vessel was equipped with a PDCR 910 (range 0–5 bar), also obtained from Druck. Two different modes of operation were adopted in the absorption experiments: one mode for aqueous piperazine solutions and the other for protonated piperazine in aqueous solution, respectively (Fig. 1).

4.1. Absorption into aqueous piperazine solutions

During all experiments that aimed at determining the kinetics of reaction (1), the reactor was operated batchwise with respect to the liquid phase and 'semi-continuous' with respect to the gas phase—as experiments were carried out at a constant (CO_2) pressure. This type of operation is preferred over a batchwise type of operation with respect to the gas phase in view of experimental accuracy: for the first reaction, the pseudo-first-order criteria indicated the requirement of a relatively low CO_2 partial pressure in the reactor. During batchwise operation with respect to the gas phase and the occurrence of a fast reaction, this would directly imply a relatively high pressure decrease (from an already low initial pressure) over a rather short period of time. A 'semi'-continuous operation makes a longer experimental period of time in the desired pseudo-first-order regime possible, thereby improving the experimental accuracy. To allow for this mode of operation, the reactor was connected to a calibrated gas supply vessel by means of a pressure controller (Brooks Instrument type 5866).

In a typical experiment, a known amount of piperazine (99%, Aldrich) was dissolved in about 600 mL of water and the solution was transferred to the liquid supply vessel, after which the liquid was degassed by applying vacuum for a short while. Next, the solution was transferred to the stirred cell, where it was allowed to equilibrate at a desired, set temperature—and the corresponding vapour pressure was recorded. Then, the pressure controller was set to the desired (total) pressure, and subsequently CO_2 (purity 99.995%, obtained from Hoekloos) was allowed to flow from the gas supply vessel to the reactor. Next, the stirrers in both phases were switched on and the pressure decrease in the gas supply vessel was recorded as a function of time. The CO_2 flux into the liquid was determined as

$$J_{CO_2} = \frac{dP_{GV}}{dt} \cdot \frac{1}{RT_{GV}A_{GL}}. \quad (17)$$

The corresponding CO_2 partial pressure in the reactor was calculated by subtracting the lean liquid's vapour pressure, determined explicitly at the beginning of the experiment, from the constant total pressure in the reactor during the experiment. The piperazine concentration was checked afterwards by volumetric titration with 1.0 N HCl.

In a typical series of experiments, the procedure above was repeated at different pressures, until—at a constant piperazine concentration and temperature—a pressure-flux curve was obtained which included the linear pseudo-first-order regime, as discussed in the previous section. In all experiments, both the liquid volume of and the stirring speed in the liquid phase, respectively, were kept constant to ensure a constant mass transfer coefficient k_L per concentration and temperature.

The maximum carbon dioxide loadings at the end of an experiment varied between 0.006 and 0.025 mol mol^{-1}, corresponding with PZ conversions of 1.2% and 5%, respectively, depending on the applied CO_2 partial pressure in an experiment. These loadings are more than a decade lower than the

loadings used by Bishnoi and Rochelle (2000) in their experimentally determined equilibrium CO_2 pressures. They reported experimental CO_2 equilibrium pressures of 32 and 42 Pa, both at a CO_2 loading of 0.32 and a temperature of 40 °C. Since these CO_2 partial pressures already are (at least) a factor of 10 lower than the CO_2 pressures applied in this work, it is justified to assume that the influence of (bulk) reverse reactions can be neglected for the experimental conditions used in the present work.

4.2. Absorption into protonated piperazine solutions

When determining the kinetics of CO_2 and protonated piperazine in an aqueous solution (reaction (3)), the setup was operated batchwise with respect to both the liquid and the gas phases. The experimental method therefore differs from the one described in the constant pressure experiments with aqueous piperazine. For these experiments, it was not necessary to follow the (relatively more) complicated procedure as described in the previous section, since the reaction rate of carbon dioxide with PZH^+ is expected to be much slower than its reaction with PZ (as explained in the Section 2), and this second—simpler—method has been found to be well applicable for systems with a low(er) kinetic rate constant. The experimental procedure applied for the determination of the kinetics of CO_2 with PZH^+ was, in fact, similar to the one described by both Blauwhoff et al. (1984) and Kumar et al. (2003), and will therefore only be briefly summarized here.

In a typical experiment, an equimolar amount of piperazine and hydrochloric acid (Aldrich) was dissolved in about 600 mL of double distilled water. HCl was chosen, since it, being a strong acid, will protonate the most basic groups in solutions irreversibly and thus convert all piperazine molecules to PZH^+. For simplicity reasons, it is assumed that the presence of the chloride ions does not influence the reaction (rate) or the mass transfer process, even though it must be noted that its concentration is identical to the PZH^+ concentration in solution. As the goal of the second set of experiments is only to validate the justification of neglecting reaction (3) with respect to reaction (1), this seems acceptable. The prepared solution was transferred to the liquid supply vessel, where vacuum was applied shortly to remove all inert gases. Then, the solution was transferred to the stirred cell reactor where it was allowed to equilibrate at the desired temperature, after which the vapour pressure was recorded. Next, pure CO_2 was fed into the reactor, the reactor was closed and the stirrers in both phases were switched on. The pressure decrease in time due to absorption of CO_2 was recorded using a computer.

If the CO_2 partial pressure above the solution is sufficiently low so that the pseudo-first-order conditions are met, the kinetics of the reaction can be determined using the following equation (Blauwhoff et al., 1984):

$$\ln(P_{CO_2,t}) = \ln(P_t - P_{vap}) = \ln(P_0 - P_{vap}) - \sqrt{k_{ov} D_{CO_2}} \frac{A_{GL}}{V_G} m_{CO_2} t. \quad (18)$$

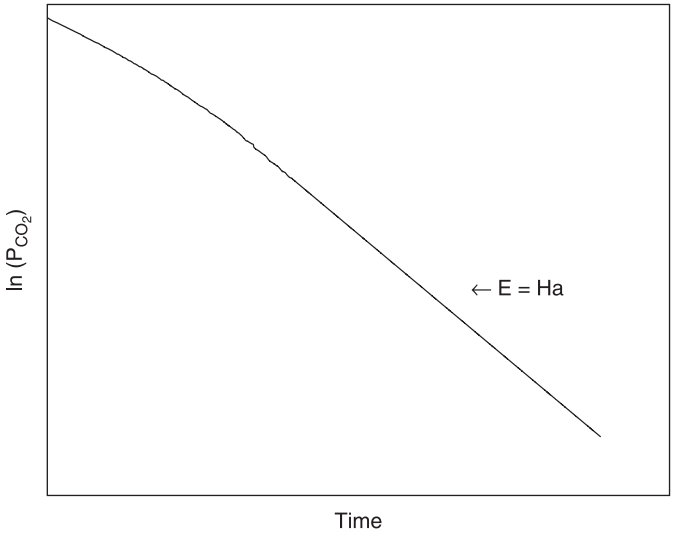

Fig. 2. Typical result of a batch experiment.

Typically, a plot of the left-hand side of Eq. (18) as function of time will yield a graph as shown in Fig. 2. If initially the pseudo-first-order conditions are not satisfied (i.e., mass transfer takes place in the instantaneous absorption regime), the slope will change in time. When the pressure has decreased sufficiently—and the pseudo-first-order conditions are satisfied—the slope will reach a constant value, from which the kinetic rate constant k_{ov} is to be determined (Eq. (18)).

Again, experimental conditions were adjusted to keep the maximum carbon dioxide loading low to minimize the influence of reversibility of the reaction. In all experiments, the loading never exceeded 0.002 mol CO_2 per mol PZH^+.

5. Results

5.1. Absorption into aqueous piperazine solutions

Experimentally determined fluxes of CO_2 at different partial pressures have been listed in Tables 3–5.

As pointed out in Section 3, only the data taken at sufficiently low CO_2 partial pressures, where a linear relation exists between the experimentally observed flux and the CO_2 partial pressure (as illustrated in Fig. 3 for two series of measurements), are to be used in the determination of the kinetic rate, as this constant slope might indicate pseudo-first-order behaviour. From the corresponding rates of absorption, the overall pseudo-first-order rate constant, k_{ov}, of reaction (1) can be calculated according to Eq. (12), thereby already assuming that the contributions of reactions (2) and (3) are negligible. It should be noted that at this point the first-order dependence of CO_2 still has not been validated, but—as already mentioned above—the fact that there seems to be a linear relation between flux and CO_2 pressure (if '$E = Ha$') is an indication that the reaction is indeed first order in carbon dioxide.

Further details as to which experimental data have been used in the kinetic rate determination are listed in Table 6, along

Table 3
Flux of CO_2 into aqueous solutions of 0.6, 1.0 and 1.5 M PZ at 20 °C

[PZ] = 0.6 M		[PZ] = 1.0 M		[PZ] = 1.5 M	
P_{CO_2} (mbar)	J_{CO_2} (mmol m^{-2} s^{-1})	P_{CO_2} (mbar)	J_{CO_2} (mmol m^{-2} s^{-1})	P_{CO_2} (mbar)	J_{CO_2} (mmol m^{-2} s^{-1})
2.53	0.632	3.72	1.07	3.95	1.29
3.34	0.79	3.89	1.20	4.64	1.50
3.68	0.91	4.11	1.11	4.92	1.64
4.26	0.98	4.12	1.20	5.88	1.88
4.72	1.11	4.40	1.30	10.5	2.90
5.96	1.32	5.31	1.45	16.1	3.99
8.22	1.69	6.00	1.70	76.4	7.14
10.9	2.02	6.25	1.67	176	8.02
13.1	2.31	7.03	1.88	277	8.46
15.8	2.55	7.90	1.98	477	9.20
36.3	3.55	7.94	1.93		
126	4.64	8.33	1.87		
262	5.16	8.33	2.08		
369	5.39	8.43	2.15		
472	5.63	8.45	2.19		
		10.7	2.47		
		10.9	2.51		
		13.5	3.29		
		13.5	3.11		
		16.1	3.35		
		16.1	3.36		
		26.1	4.16		
		26.2	4.16		
		36.0	4.51		
		36.2	4.68		
		75.7	6.01		
		102	6.32		
		172	6.94		
		252	7.11		
		252	7.16		
		352	7.66		
		352	7.53		
		402	7.67		
		406	7.60		
		472	7.79		

with the required physical properties and calculation results. The listed physical properties are, in fact, the distribution and diffusion coefficients of N_2O in aqueous PZ solutions, and they were converted to the corresponding CO_2 values using the well-known and widely applied N_2O: CO_2 analogy (the reader is referred to Versteeg and Van Swaaij, 1988b for the conversion equations).

Before drawing conclusions from Table 6, it needs to be verified if the pseudo-first-order conditions (Eq. (11)) have been satisfied in these experiments. A list of governing Hatta numbers and corresponding (irreversible) infinite enhancement factors (according to Eq. (10)) are listed in Table 7. The diffusion coefficient of piperazine— necessary in the calculation of the infinite enhancement factor—was estimated using the diffusion coefficient of MDEA, corrected for the molecular weight by multiplying with a factor of 1.38. The diffusion coefficient of MDEA as a function of temperature and concentration was calculated with the experimentally derived equation given by Snijder et al. (1993):

$$\ln D_{\mathrm{MDEA}} = -13.808 - \frac{-2360.7}{T} - 24.727 \times 10^{-5}[\mathrm{MDEA}]. \quad (19)$$

Table 7 clearly shows that in all cases the *Ha* number is more than substantially larger than two, and that the ratio between the infinite enhancement factor and the Hatta number is about a factor of 4. Pseudo-first-order behaviour is, however, only really ensured at ratios between E_{inf} and *Ha* of least a factor of 10, so with a factor of 4 it might be necessary not only to interpret the results according to Eq. (12) ('pseudo-first-order regime') but also with the help of Eq. (13) ('intermediate regime'). The ratio between E_{inf} and *Ha* could not be increased by further lowering the CO_2 partial pressure, because the error in the determination of the CO_2 partial pressure (which is needed in the interpretation of the experiments) would become unacceptable. This is because the CO_2 partial pressure is indirectly

Table 4
Flux of CO_2 into aqueous solutions of 0.6, 1.0 and 1.5 M PZ at 25 °C.

[PZ] = 0.6 M		[PZ] = 1.0 M		[PZ] = 1.5 M	
P_{CO_2} (mbar)	J_{CO_2} (mmol m^{-2} s^{-1})	P_{CO_2} (mbar)	J_{CO_2} (mmol m^{-2} s^{-1})	P_{CO_2} (mbar)	J_{CO_2} (mmol m^{-2} s^{-1})
3.15	0.77	3.44	1.01	3.77	1.26
3.62	0.96	3.48	0.98	4.34	1.4
3.94	0.875	3.92	1.14	4.84	1.57
4.15	1.02	4.28	1.34	5.25	1.73
4.37	1.03	4.36	1.37	6.22	1.92
4.86	1.15	5.07	1.39	7.27	2.41
5.50	1.29	6.1	1.67	7.94	2.35
6.48	1.39	6.82	1.82	10.4	3.17
6.92	1.55	6.88	2.04	18.5	4.84
7.06	1.63	7.25	2.02	26.7	5.85
8.09	1.98	7.39	2.14	68	8.29
14.2	2.68	10.4	2.61	195	9.81
22.2	3.35	10.6	2.72	345	10.5
27.0	3.71	10.8	2.66	468	10.9
75.8	4.85	19.5	4.00		
128	5.41	19.6	4.13		
128	5.43	28.6	4.82		
243	5.92	143	7.83		
343	6.08	244	8.19		
343	6.13	419	8.79		
415	6.20	463	9.04		
463	6.46				
463	6.53				

Table 5
Flux of CO_2 into aqueous solutions of 1.0 M PZ at 30 and 40 °C

T = 30 °C		T = 40 °C	
P_{CO_2} (mbar)	J_{CO_2} (mmol m^{-2} s^{-1})	P_{CO_2} (mbar)	J_{CO_2} (mmol m^{-2} s^{-1})
4.14	1.28	5.31	1.69
4.71	1.48	5.32	1.69
5.32	1.56	5.60	1.64
6.14	1.88	5.86	2.03
6.56	1.93	6.40	2.08
8.21	2.37	6.55	1.86
9.5	2.63	6.78	2.09
11.9	3.28	7.93	2.30
14.0	3.49	8.29	2.46
31.6	5.93	8.54	2.43
55.1	7.5	10.7	3.1
156	9.07	12.2	3.53
233	9.44	16.2	4.53
308	9.94	20.3	4.99
433	10.7	25.9	5.82
		42.1	7.27
		60.7	8.99
		101	9.98
		136	11.3
		178	11.1
		179	11.1
		228	12.1
		278	12.3
		338	12.5
		403	12.9

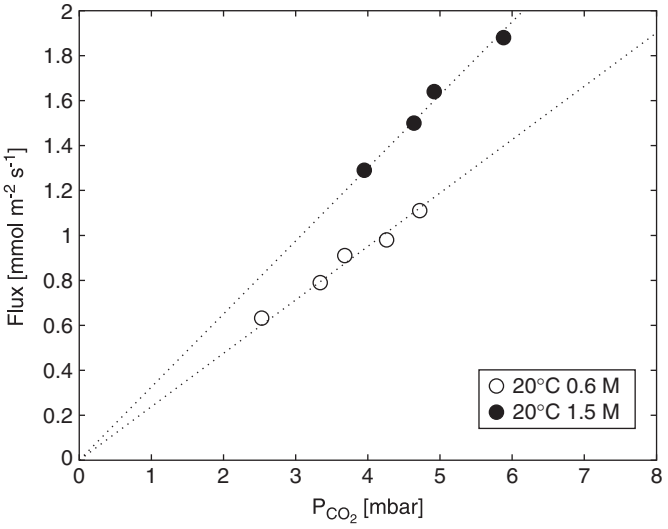

Fig. 3. Two series of experimentally observed fluxes, apparently measured in the pseudo-first-order regime.

determined by the difference between the actual reactor pressure and the vapour pressure of the fresh solution. At low CO_2 partial pressures, the difference between the actual pressure and the vapour pressure is relatively small as compared to the actual pressure and the relative error in the determination of the CO_2 partial pressure thus increases rapidly below $P_{CO_2} \simeq 4$ mbar (400 Pa). When using Eq. (13), the

Table 6
Kinetic data for the reaction of CO_2 with piperazine in aqueous solutions

Temp. (K)	Conc. (kmol m^{-3})	N[a] (–)	Slope[b] (mmol m^{-2} s^{-1} mbar^{-1})	m_{N_2O}[c] (–)	D_{N_2O}[d] ($\times 10^{-9}$ m^2 s^{-1})	k_{ov} ($\times 10^3$ s^{-1})
293.15	0.6	5	0.238	0.669	1.30	29.4
293.15	1.0	7	0.285	0.662	1.12	50.3
293.15	1.5	4	0.325	0.637	0.95	82.8
298.15	0.6	7	0.239	0.590	1.51	33.6
298.15	1.0	11	0.285	0.584	1.31	56.2
298.15	1.5	4	0.327	0.564	1.10	94.0
303.15	1.0	5	0.302	0.493	1.73	68.1
313.15	1.0	5	0.321	0.429	2.15	85.3

[a]Number of experimental data used in determining kinetics, taken from Tables 3–5.
[b]Average dJ/dp slope over those N points.
[c]The values for the distribution coefficient were taken from Derks et al. (2005b) (20 and 25 °C) and Sun et al. (2005) (30 and 40 °C).
[d]The diffusion coefficients at 30 and 40 °C were taken from Sun et al. (2005). Diffusion coefficients at 20 and 25 °C were estimated using a modified Stokes–Einstein equation as shown in Appendix B.

Table 7
Calculated *Ha* numbers and corresponding (infinite) enhancement factors

Temp. (K)	Conc. (kmol m^{-3})	$k_{L,0}$ (m s^{-1})	k_{ov} ($\times 10^3$ s^{-1})	*Ha* (–)	P_{CO_2} (mbar)	D_{PZ} ($\times 10^{-9}$ m^2 s^{-1})	E_{inf}[a] (–)
293.15	0.6	2.02	29.4	320	4.72	0.79	1286
293.15	1.0	1.69	50.3	465	6.00	0.71	1748
293.15	1.5	1.42	82.8	651	5.88	0.63	2833
298.15	0.6	2.23	33.6	331	5.50	0.90	1256
298.15	1.0	1.98	56.2	449	7.39	0.81	1606
298.15	1.5	1.69	94.0	628	5.25	0.72	3591
303.15	1.0	2.31	68.1	486	6.56	0.93	2010
313.15	1.0	2.97	85.3	465	6.40	1.19	2455

[a]Same m and D as used in calculations in Table 6.

Table 8
Results of the reinterpretation of the experimental data based on the DeCoursey approximation.

Temp. (K)	Conc. (kmol m^{-3})	N[a] (–)	*Ha*-DC[b] (–)	k_{ov}-DC ($\times 10^3$ s^{-1})	*Ha*-PFO[c] (–)	k_{ov}-PFO ($\times 10^3$ s^{-1})
293.15	0.6	10	350	35.2	320	29.4
293.15	1.0	25	501	58.5	465	50.3
293.15	1.5	6	712	98.9	651	82.8
298.15	0.6	13	373	42.7	331	33.6
298.15	1.0	17	499	69.4	449	56.2
298.15	1.5	11	676	108.9	628	94.0
303.15	1.0	10	550	87.2	486	68.1
313.15	1.0	18	491	95.3	465	85.3

[a]Number of data points used in the calculation of the average *Ha* number.
[b]The Hatta number as a result from the data regression.
[c]The Hatta number assuming pseudo-first-order behaviour (Table 7).

kinetics are derived by using the *Ha*-number as a fitting parameter so that the enhancement factor calculated using Eq. (13) matches the experimentally observed enhancement factor. For this procedure only data that matched the criterion '$E_{inf} > 1.2 \cdot E_{exp}$' were used, therewith excluding data with a low sensitivity towards the kinetics. The accordingly obtained results are listed in Table 8.

Table 8 shows that the determination of the kinetics using Eq. (13) yields a larger overall kinetic rate constant (10–30%), which was to be expected following the conclusions drawn

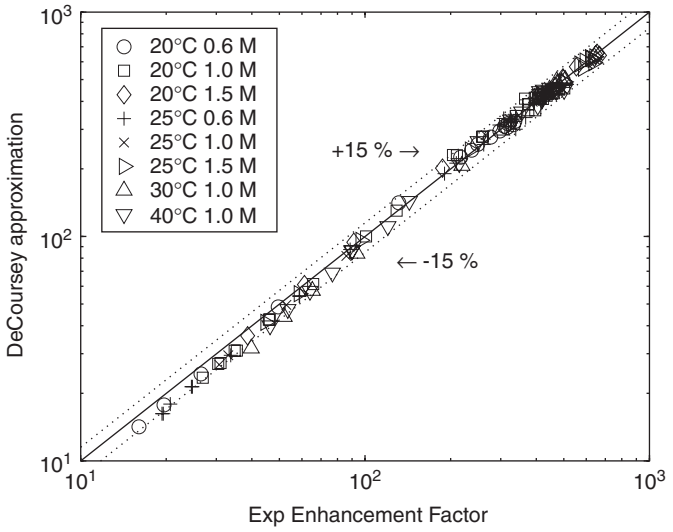

Fig. 4. Parity plot of experimental enhancement factor and the DeCoursey approximation using the irreversible infinite enhancement factor.

before concerning the pseudo-first-order conditions. These results obtained from the analysis based on Eq. (13) will be used in all following discussions and conclusions.

A graphical representation between all experimentally observed enhancement factors and the calculated enhancement factors based on the DeCoursey approximation—using the kinetics as listed in Table 8, and all physical constants as listed in Table 6—is given in Fig. 4.

Fig. 4 shows that for all experimental absorption rates listed in Tables 3–5, experimental values and predictions calculated from the DeCoursey equation are in good agreement with each other. Deviations between model and experiment might be attributed to, among others, the estimated diffusion coefficients for both CO_2 and piperazine.

Before elaborating further on the results, first the assumption concerning the (ir)reversibility of the reaction should be validated. It was stated earlier that reaction (1) could be regarded irreversible based on the relatively high value for the equilibrium constant and the very low CO_2 loadings applied in this work. Therefore, in Table 9 the infinite enhancement factor adapted for reversibility according to Secor and Beutler (1967) and modified for the penetration theory as suggested by Hogendoorn et al. (1997) is listed and compared to the irreversible infinite enhancement factor as presented earlier in Table 8. The governing equations and definitions as well as a calculation example are given in Appendix B.

As the difference between both the reversible and irreversible infinite enhancement factors never exceeds 10–20%, it is fairly safe to state that reversibility only has a marginal influence on the actual kinetics experiments: the maximum deviation in the overall kinetic rate constant between using the irreversible and the reversible infinite enhancement factor is 10%, observed at 313.15 K. It should be noted here that the use of this approximation method introduces an error in the obtained overall kinetic rate constant. However, for the conditions applied in this work, the average deviation between the approximated result and the exact numerical solution is always less than 5% (Hogendoorn et al., 1997).

Now, a closer look is given to the results presented in Table 8. The data obtained at different PZ concentrations at 20 and 25 °C are to be used to identify the mechanism of the reaction of piperazine with CO_2. Usually, a log–log plot of the apparent kinetic rate k_{ov} versus the amine concentration is made to investigate which of the asymptotic cases described in Section 2 are valid: the reaction order with respect to the amine is given directly by the slope of the graph. A log–log plot of the present data at 20 and 25 °C yields a reaction order with respect to piperazine of about 1.0–1.3. However, considering the uncertainty with respect to the CO_2 diffusion coefficient, the reaction order with respect to PZ is assumed to be one at this stage, also based on the following considerations:

- Based on the literature on the kinetics between CO_2 and a wide variety of aqueous (alkanol)amines, it seems fair to assume that the reaction order with respect to CO_2 is one.
- Both previous studies on the kinetics between CO_2 and aqueous PZ have reported a partial reaction order of piperazine of one.

Now, the corresponding k_2 rate constants are calculated from the apparent kinetic rate k_{ov} resulting from the DeCoursey relation (based on an irreversible enhancement factor) as listed in Table 8, based on the considerations above, and the resulting values are listed in Table 10.

The obtained k_2 values at 20 and 25 °C seem to support the assumption with respect to the reaction order of piperazine, since the value per temperature is more or less constant (within 10%) over the concentration range studied. Had the assumption been false, a much larger effect of the concentration on the kinetic rate constant k_2 would have been expected. Therefore, an overall second-order reaction rate according to Eq. (4) (with the corresponding k_2 constants as determined in Table 10) is assumed in all further calculations and discussions.

In summary, this last paragraph has provided three different methods to interpret the experimentally obtained absorption rates, all of which are based on a (more or less) different principle—as pointed out in Table 11.

As already shown in Tables 6, 8 and 9, these different interpretation techniques can lead to different kinetic rate constants. A schematic overview of the results is given in Table 12, where the forward kinetic rate constants k_2 have been determined assuming first-order dependence in piperazine (see Table 10).

The results obtained with the DeCoursey relation (based on an irreversible enhancement factor) are considered to be the most accurate, since, on one hand, the pseudo-first-order criteria are probably not fully satisfied (see results listed in Table 7). On the other hand, the effect of reversibility on the results is so small that it does not outweigh the extra uncertainties that

Table 9
Reversible and irreversible infinite enhancement factors

Temp. (K)	Conc. (kmol m^{-3})	P_{CO_2} (mbar)	$E_{inf,irrev}$ [a] (–)	$E_{inf,rev}$ [b] (–)	k_{ov} (irrev) ($\times 10^3$ s^{-1})	k_{ov} (rev) ($\times 10^3$ s^{-1})
293.15	0.6	4.72	1286	1164	35.2	36.9
293.15	1.0	6.00	1748	1600	58.5	61.4
293.15	1.5	5.88	2833	2592	98.9	102.2
298.15	0.6	5.50	1256	1112	42.7	45.5
298.15	1.0	7.39	1606	1447	69.4	72.6
298.15	1.5	5.25	3591	3179	108.9	114.9
303.15	1.0	6.56	2010	1736	87.2	93.7
313.15	1.0	6.40	2455	1942	95.3	104.1

[a]Same m and D as in Table 6.
[b]See Appendix B for governing equations and calculation example.

Table 10
Second-order kinetic rate constants

Temp. (K)	Conc. (kmol m^{-3})	k_{ov} ($\times 10^3$ s^{-1})	k_2 (m^3 kmol^{-1} s^{-1})
293.15	0.6	35.2	59
293.15	1.0	58.5	59
293.15	1.5	98.9	66
298.15	0.6	42.7	71
298.15	1.0	69.4	69
298.15	1.5	108.9	73
303.15	1.0	87.2	87
313.15	1.0	95.3	95

Table 11
Methods used to interpret experimental data

Method	Enhancement factor from		Infinite enhancement factor	
First order	$E = Ha$	Eq. (12)	Irreversible	Eq. (10)
DeCoursey relation	$E \propto (Ha, E_{inf})$	Eq. (13)	Irreversible	Eq. (10)
Hogendoorn approximation	$E \propto (Ha, E_{inf})$	Eq. (13)	Reversible	Eq. (B.6)

Table 12
Second-order kinetic rate constants according to the interpretation methods applied

Temp. (K)	k_2[a] (m^3 kmol^{-1} s^{-1})		
	PFO	DeCoursey	Hogendoorn
293.15	52	61	64
298.15	58	71	75
303.15	68	87	94
313.15	85	95	104

[a]For 20 and 25 °C, the average k_2 values over the three concentrations are listed.

are introduced when applying Hogendoorn's approach, which requires the equilibrium constant of the reactants as well as the diffusion coefficients of all reaction products.

5.2. *Kinetics of* CO_2 *with protonated piperazine*

As discussed in Section 2, the assumption concerning the supposedly negligible relative contribution of reaction (3) to the overall mass transfer rate needs experimental validation. As information concerning the order of magnitude will do in this respect, experiments have been limited to a temperature of 25 °C and a concentration of about 1.0 kmol m^{-3} PZH^+. Since PZH^+ itself is the strongest base present in solution (as all other bases such as PZ and OH^- have been neutralized by the (excess) HCl), the overall reaction can be described according as

$$CO_2 + 2PZH^+ \rightleftarrows H^+PZCOO^- + PZH_2^{2+}. \quad (20)$$

As in the reaction of piperazine with CO_2, it also assumed that the formation of the zwitterion is the rate determining step in Eq. (20) (reaction (3)), characterized by a second-order kinetic rate constant k_2, as the reaction is assumed to react first order in both CO_2 and PZH^+:

$$CO_2 + PZH^+ \overset{k_2}{\rightleftarrows} H^+PZH^+COO^-. \quad (21)$$

Absorption experiments into these protonated piperazine solutions ($[PZH^+] = 0.99$ kmol m^{-3}) were performed with a batchwise operated gas phase and at initial CO_2 partial pressures of about 40–45 mbar. Apparent pseudo-first-order behaviour—a straight slope according to Eq. (18) (see Fig. 2)—was found at pressures below about 15 mbar CO_2. Experiments were carried out at different liquid stirrer speeds to validate the assumption concerning operating in the pseudo-first-order regime, where the stirrer speed (or the mass transfer coefficient k_L) should not influence the flux. Results of the kinetic experiments are listed in Table 13.

Table 13
Experimental results on the kinetics of the reaction between CO_2 and PZH^+, applying batchwise operation of the set-up

N (min^{-1})	k_L[a] ($\times 10^{-5}$ m s^{-1})	$10^6\sqrt{k_{ov} \cdot D}$[b]	Enhancement factor[c]
48.60	1.20	346	29.0
73.1	1.59	412	25.9
90.4	1.85	481	26.0
106.5	2.07	498	24.1
122.6	2.28	527	23.1

[a]$k_L \propto N^{0.7}$.
[b]The slope has been interpreted assuming that '$E = Ha$' was valid.
[c]$E = \sqrt{k_{ov} \cdot D}/k_L$.

Table 14
Flux of CO_2 into an aqueous solutions of 1.0 M PZH^+ at 25 °C, applying a 'semi-continuous' operation of the set-up

Reactant	N (min^{-1})	k_L ($\times 10^{-5}$ m s^{-1})	P_{CO_2} (mbar)	J_{CO_2} (mmol m^{-2} s^{-1})	Enhancement factor (–)
PZH^+	49.2	1.22	12.9	0.14	28.1
			23.0	0.23	25.0
			34.6	0.30	21.8
	72	1.59	14.1	0.19	26.1
			24.1	0.29	23.3
			34.3	0.37	20.9
	95.8	1.94	14.3	0.22	25.0
			24.3	0.33	22.0
			34.5	0.43	19.9
PZ		1.98	10.8	2.66	
			19.5	4.00	

It is obvious from the results that the observed apparent kinetic rate term $k_{ov} \cdot D$ does not reach a constant value with increasing stirrer speed and physical mass transfer coefficient k_L (i.e., decreasing Ha number), which implies that the experiments have not (completely) been carried out in the pseudo-first-order regime. The (rather large) influence of the k_L on the observed results might be explained by the reversibility of the reaction (between PZH^+ and CO_2), which—depending on the value of the equilibrium constant—can lower the infinite enhancement factor.

This hypothesis was checked by performing some 'semi-continuous' experiments at different stirrer speeds and CO_2 partial pressures following the same method as used for aqueous piperazine solutions. Observed experimental fluxes were then compared to the fluxes obtained with aqueous piperazine solution at similar conditions (see also Table 4).

From Table 14, two conclusions can be drawn. Firstly, the enhancement factors observed in the experiments with 14 mbar CO_2 partial pressure are similar to the ones observed in the batch experiments at comparable stirrer speed, which means both experimental methods and results are consistent. Secondly, the experimentally determined CO_2 fluxes into the protonated piperazine solutions are at least one order of magnitude lower than the absorption rate into the piperazine solutions at similar conditions. Under the previously mentioned assumption of a second-order rate determining formation of the zwitterion (see Eq. (21)) and an equilibrium constant value in the PZH^+ system which is in the same order of magnitude as in the piperazine system, this would imply a considerably lower kinetic rate and hence pseudo-first-order criteria should be more easily obeyed. As this is obviously not the case, it means that the absorption of CO_2 into protonated piperazine solutions could be influenced by the reversibility of the reaction between carbon dioxide and PZH^+. An indication towards the occurrence of reversibility is the magnitude of the equilibrium constant of the reaction, which—according to the overall reaction given in Eq. (20)—is defined as follows:

$$K_{eq} = \frac{[^+HPZCOO^-][PZH_2^{2+}]}{[CO_2][PZH^+]^2}. \quad (22)$$

Its value can be calculated similar to Eq. (16), using the equilibrium constants as determined by Ermatchkov et al. (2002) and Hetzer et al. (1967), and is found to be 1.6 m^{-1}. This value is four orders of magnitude smaller than the equilibrium constant as determined for the reaction between piperazine and CO_2 ($K_{Eq} = 8 \times 10^4$ m^{-1}, see Table 1) and therefore it supports the hypothesis with regard to the influence of reversibility.

Now, to interpret the experimental results, a similar approach is followed as for the experimental data for the absorption into aqueous piperazine: the infinite enhancement factor, adjusted to account for reversibility (Hogendoorn et al., 1997; Secor and Beutler, 1967), for the PZH^+ system is calculated, and the 'equilibrium adapted' DeCoursey relation (or the 'Hogendoorn approximation' in Table 11) is then applied to calculate the enhancement factor (see Appendix B for all governing equations). The forward kinetic rate constant, k_2 in Eq. (21), which is necessary in the determination of the Ha number, is used as the (single) adjustable parameter to match experiment and model.

All other necessary parameters were estimated as follows:

- All physicochemical constants were assumed to be identical to the properties listed for the 1.0 M piperazine solution at 298.15 K in Tables 6 and 7.
- The diffusivity of all piperazine species is assumed to be identical.

The results of this procedure to fit the kinetic rate constant to the experiments are plotted in Fig. 5.

Fig. 5 shows that Hogendoorn's approximation method used here is able to describe the experimentally obtained results well, and, since the predicted results were (still) susceptible to (changes in) the guessed value for the forward kinetic rate constant, this constant could indeed be used as an adjustable parameter in the correlation of the experimental results. The fitted second-order forward kinetic rate constant was found to have a value of (0.28 ± 0.10) m^3 mol^{-1} s^{-1} at 298.15 K. Although this is merely a global estimation based on an approximation method, it does provide a possibility to quantitatively compare the forward kinetic rate constants of reactions (1) and (3) between CO_2 and piperazine or its protonated species. The latter

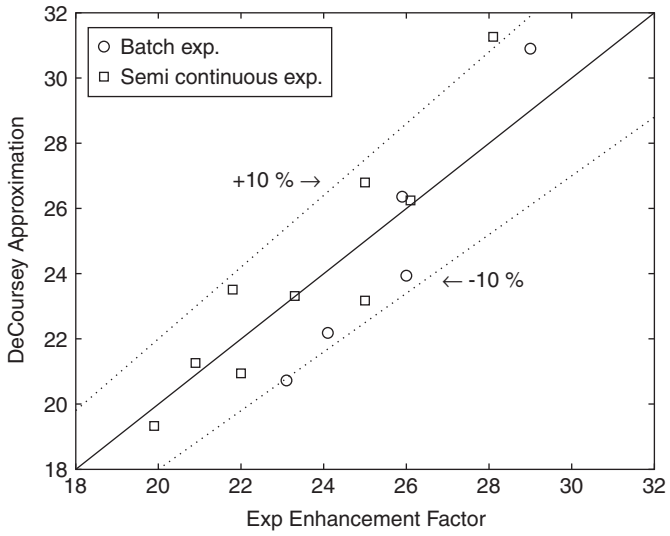

Fig. 5. Comparison of the experimentally observed enhancement factors in the CO_2–PZH^+ system with the theoretical prediction based on the Hogendoorn approximation method.

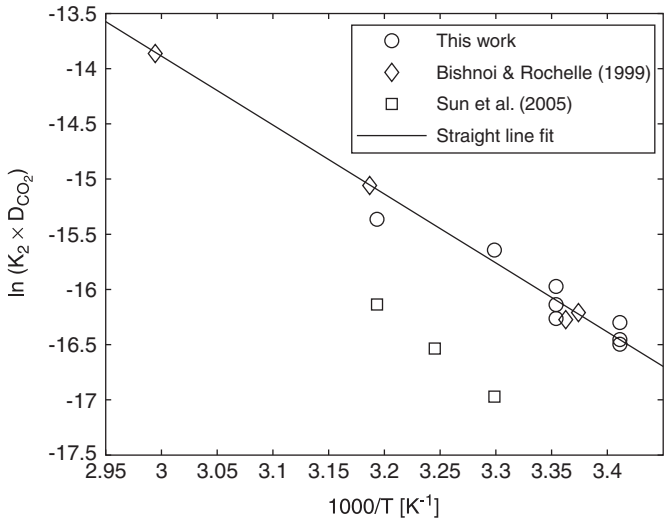

Fig. 6. The Arrhenius plot of the product $(k_2 \cdot D_{CO_2})$ for the reaction of CO_2 with piperazine in aqueous solution. The straight line fit neglects the data of Sun et al. (2005).

was found to be about two orders of magnitude smaller than the former, under the assumption with regard to the rate determining step being the formation of the zwitterion (Eqs. (20), (21)), thereby validating the assumption concerning the neglect of reaction (3) in the determination of the reaction rate between piperazine and CO_2 in aqueous environment in—or near—the '$E = Ha$' regime.

6. Discussion

It is demonstrated in this work—both by the qualitative analysis in Section 2 and the quantitative results on the absorption of CO_2 into aqueous solutions of protonated piperazine—that experimental data on the absorption of CO_2 into aqueous piperazine solutions in or near the '$E = Ha$' regime can be interpreted by means of assuming the single presence of the reaction between CO_2 and piperazine. The contribution of reactions of other species present (e.g. OH^- and PZH^+) can correctly be neglected.

A comparison between the present data, interpreted with the DeCoursey relation (based on an infinite enhancement factor, see Table 8 and the kinetic rate data presented by Bishnoi and Rochelle, 2000; Sun et al., 2005) is given in the Arrhenius plot in Fig. 6. Due to lack of experimental diffusion coefficient data, and to avoid the comparison being influenced too much by the used estimation method for the diffusion coefficients, it is not the second-order kinetic rate constant k_2 that is plotted on the y-axis, but this rate constant multiplied with the diffusion coefficient of CO_2, $k_2 \cdot D_{CO_2}$.

Fig. 6 illustrates that the present data are well in line with the experimental values reported by Bishnoi and Rochelle (2000), and, simultaneously, that there is a distinct deviation between these first two data sets and the kinetic data presented by Sun et al. (2005). Sun et al. (2005) found much lower values than the data reported in the work of Bishnoi and Rochelle (2000) and the present study. An explanation could be that the pseudo-first-order conditions may not have been satisfied in their work: absorption experiments by Sun et al. (2005) have been carried out at CO_2 partial pressures ranging from 32 to 77.5 mbar, which is a factor of 6–10 higher than the maximum CO_2 pressures as listed in Table 7 (resulting in E_{inf} values that are a factor of 6–10 lower than in this work), while the mass transfer coefficient k_L is less than a factor of 3 higher than in the current work, leading to Ha numbers which are less than a factor of 3 lower than in this work. As a result, the ratio between the Ha number and the infinite enhancement factor is a factor of 2–3 lower than in this work while they still interpret their experiments as if they were conducted in the pseudo-first-order regime, which seems not completely justified. Besides this, there appears to be an inconsistency in the work by Sun et al. (2005): they report the CO_2 diffusion coefficients in aqueous PZ solutions to be smaller than the experimentally determined diffusion coefficients of N_2O, which seems contradictory to the CO_2:N_2O analogy: at the temperatures in their work, the diffusion coefficient of CO_2 should exceed the diffusion coefficient of N_2O. Moreover, the self-diffusion coefficient of an amine in its aqueous solution decreases with increasing concentration (due to an increasing liquid viscosity); Sun et al. (2005) report a contradictory behaviour.

Bishnoi and Rochelle (2000) performed their absorption experiments in a wetted wall contactor at conditions (a mass transfer coefficient $k_L > 10^{-4}$ m s^{-1} and CO_2 partial pressure < 2 mbar) which seem to ensure a pseudo-first-order behaviour. Their experimental results are in good agreement with the present data, with the exception of the data at 313 K. This is partly due to the effect of reversibility of the reaction on our experimental results at this temperature. As the results in Table 9 already illustrated, incorporation of reversibility in the determination of the kinetic rate constant shows the highest

Table 15
Kinetic rate constants and pK_a values at 25 °C for some selected (alkanol)amines

Amine[a]	pK_a[b]	Source	k_2[c]	Source
MEA	9.50	Perrin (1965)	6.0	Versteeg et al. (1996)
DGA	9.47	Littel et al. (1990)	4.5	Versteeg et al. (1996)
DEA	8.92	Perrin (1965)	1.3	Versteeg et al. (1996)
DIPA	8.88	Kim et al. (1987)	0.1	Versteeg et al. (1996)
MMEA	9.80	Littel et al. (1990)	7.1	Versteeg et al. (1996)
Piperazine	9.73	Hetzer et al. (1967)	70/59	This work, Bishnoi and Rochelle (2000)
Piperazine-H^+	5.33	Hetzer et al. (1967)	0.28	This work
Piperidine	11.12	Perrin (1965)	60.2	Sharma (1965)
Morpholine	8.36	Perrin (1965)	18/20.5	Sharma (1965) and Alper (1990)
Aminoethyl-PZ	9.48	Perrin (1965)	28.0	Bishnoi (2002)
Hydroxyethyl-PZ	9.38	Castro et al. (1997)	11.0	Bishnoi (2002)
Aniline	4.61	Perrin (1965)	0.051	Sharma (1965)
Benzylamine	9.34	Perrin (1965)	8.51	Sharma (1965)
Cyclohexylamine	10.68	Perrin (1965)	8.2	Sada et al. (1986)

[a]Subdivided into (ordinary) primary and secondary alkanolamines, piperazine-like molecules and cyclic amines with the NH_2-group outside the ring structure.
[b]Some of the pK_a values stem from interpolating the available data at different temperatures.
[c]Some of the listed k_2 constants have been obtained via extrapolation of experimental data taken at different temperatures.

deviation at $T = 313.15$ K. Since this data point at 313 K from the present work seems to deviate from the trend set by all other data points from both the present work and the work of Bishnoi and Rochelle (2000), it was decided to omit this data point from the Arrhenius fit. The temperature dependence of the product of the forward second-order kinetic rate constant and the diffusion coefficient is then described as

$$k_{2,\mathrm{PZ-CO_2}} \cdot D_{\mathrm{CO_2}} = 128.4 \exp\left(-\frac{6.2 \times 10^3}{T}\right). \quad (23)$$

Usually, the apparent activation temperature of the diffusion coefficient of CO_2 in aqueous (amine) solutions is in the order of 2.1 K (see e.g. Versteeg et al., 1996), and hence it seems safe to state that the activation temperature of the reaction amounts to (4.1 ± 0.3) K.

As already mentioned in Section 2, the Brønsted plot technique has shown that for various groups of aqueous alkanolamines, there is a (linear) relation between the pK_a value of an (alkanol)amine and (the logarithm of) the forward rate constant (Versteeg et al., 1996). It would be interesting to investigate whether there also exists a similar relation for amines which resemble piperazine. If this would be the case, such a Brønsted plot can be used for the prediction of the kinetic rate of other amines, and hence it might serve as a tool in designing new activators. Table 15 lists the pK_a value and the corresponding second-order kinetic rate constant k_2 for a selection of amines at a temperature of 25 °C. The corresponding Brønsted plot is shown in Fig. 7.

Fig. 7 indicated that a kind of Brønsted relationship also exists for amines with a ring structure similar to piperazine. Although some of the data plotted in Fig. 7 are in fact estimates derived via extrapolation from different temperatures, the results seem very promising. According to this plot, the forward

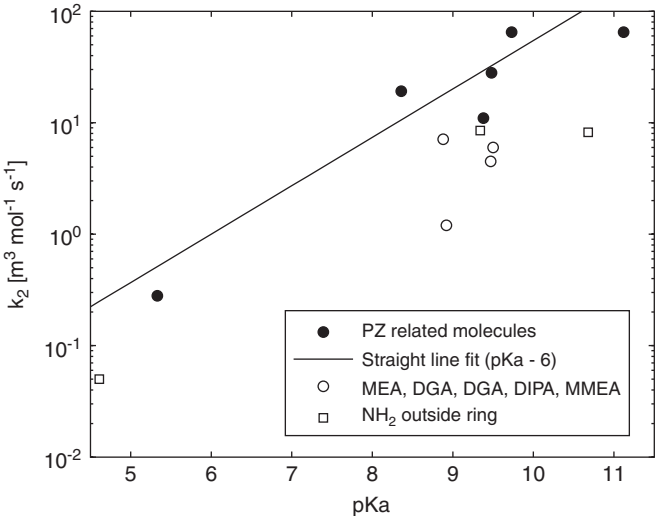

Fig. 7. Brønsted plot for piperazine and related molecules at 25 °C.

kinetic rate constant of a piperazine alike molecule with CO_2 at a temperature of 25 °C can be estimated based on the corresponding pK_a value as

$$\ln k_2 = pK_a - 6. \quad (24)$$

For the carbamated piperazine ($PZCOO^-$), with a pK_a of 9.44, this would imply a kinetic rate constant of 31 m^3 mol^{-1} s^{-1} at 25 °C. This does not mean that this reaction affects the outcome of the interpretation of the kinetic study in the present work, since the $PZCOO^-$ concentration is negligibly low (always smaller than 0.04 kmol m^{-3}), but under other experimental/industrial conditions, such as high CO_2 partial pressure and loading, this reaction is expected to make a (noticeable) contribution to the absorption rate. Of course, it must be kept in

mind that this analysis is based on the use of a Brønsted relation, and, although the first results with this limited group of piperazine based amines indicate that the Bronsted relation is applicable, information on more piperazine related amines (especially in the pK_a range of 6–8) is needed to investigate this relation more thoroughly.

7. Conclusion

Aqueous (blends of) amine solutions are frequently used solvents for the removal of acid gas components from industrial gas streams. Particularly, the piperazine activated aqueous *N*-methyldiethanolamine solution has become subject of research since it has proven to be a very promising blend in the bulk removal of carbon dioxide. Although the kinetics of MDEA with carbon dioxide have been studied extensively in the past, only two studies report (mutually strongly deviating) kinetic rate data concerning the reaction between piperazine and CO_2 in aqueous solutions. In the present work, a stirred cell setup was used to obtain and report new absorption rate data of CO_2 into aqueous piperazine solutions at different PZ concentrations, CO_2 partial pressures and temperatures. Three different interpretation methods were used to extract the rate constants of the reaction between piperazine and carbon dioxide from the obtained experimental data. First of all, the pseudo-first-order principle was used, where the enhancement factor equals the Hatta number. Secondly, the DeCoursey relation was used, which gives the enhancement factor as an explicit function of *Ha* and the (irreversible) infinite enhancement factor and thirdly, the Hogendoorn approximation was applied, which comprises the DeCoursey relation with an infinite enhancement factor which is corrected for the reversibility of the reaction. As the pseudo-first-order conditions were probably not fully satisfied and since the effect of reversibility was found to be negligibly small, the DeCoursey equation was considered to be the most suitable method to deduct the kinetic rate constants from the experimental results. The second-order kinetic rate constant for the reaction between piperazine and carbon dioxide as obtained with this DeCoursey relation was found to be in good agreement with the kinetic rate data reported by Bishnoi and Rochelle (2000). The values presented by Sun et al. (2005) are considerably lower, which is probably due to the fact that pseudo-first-order conditions have not been completely satisfied in their work. The reaction between piperazine and CO_2 in aqueous solutions seems to be an overall second-order reaction, which implies instantaneous deprotonation of the zwitterion as typically found for reactions between CO_2 and primary alkanolamines. However, it should be noted that this finding is partly based on the use of estimated diffusion coefficients, and, therefore, experimental diffusivity data should become available to finally confirm this. Finally, also the absorption of CO_2 into partially protonated piperazine solutions was experimentally investigated. Again, it was found that pseudo-first-order conditions could not be satisfied, mainly because of the relatively low equilibrium constant for this reaction. The observed experimental enhancement factors were therefore interpreted using the Hogendoorn approximation, hence using an infinite enhancement factor which is corrected for the reversibility of the reaction. The second-order kinetic rate constant was found to be approximately $0.28\,m^3\,mol^{-1}\,s^{-1}$.

Notation

A_{GL}	gas–liquid interfacial area, m^2
C	concentration, $mol\,m^{-3}$
D	diffusion coefficient, $m^2\,s^{-1}$
J	flux, $mol\,m^{-2}\,s^{-1}$
k	kinetic rate constant, $m^3\,mol^{-1}\,s^{-1}$
K	equilibrium constant
m	distribution coefficient
P	pressure, Pa
R	gas constant, $8.314\,J\,mol^{-1}\,K^{-1}$
t	time, s
T	temperature, K or °C
V	volume, m^3

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Appendix A. Diffusion coefficient of CO_2 used in the determination of kinetic constants

In the determination of the kinetic rate constant from experimental absorption rate results the diffusion coefficient of CO_2 in aqueous piperazine solutions is required. As CO_2 reacts with piperazine, its diffusion coefficient is not independently measurable, and therefore this property was indirectly estimated from the diffusivity of N_2O in aqueous piperazine solutions.

Sun et al. (2005) experimentally determined the N_2O diffusion coefficient in aqueous piperazine solutions at various concentrations for temperatures of 30, 35 and 40 °C. Their data at a piperazine concentration of $0.92\,kmol\,m^{-3}$ have been used in the interpretation of the kinetic rate experiments at 30 and 40 °C performed in this work.

The N_2O diffusivities at temperatures of 20 and 25 °C have been estimated using the modified Stokes–Einstein equation proposed by Versteeg and Van Swaaij (1988b). Eq. A.1 was found to give satisfactory results in estimating the N_2O diffusivity in various aqueous alkanolamine solutions at different temperatures:

$$(D_{N_2O} \cdot \eta^{0.8})_{PZ\,sol} = \text{constant} = (D_{N_2O} \cdot \eta^{0.8})_{water}. \qquad (A.1)$$

Viscosities of piperazine solutions at different temperatures and PZ concentrations have been experimentally determined by Derks et al. (2005b). Viscosities of water as a function of temperature are listed in Lide (1994), and the diffusion coefficient of N_2O in water was calculated from the equation presented

Table A.1
Estimation of CO_2 diffusion coefficients

T (K)	η_{H_2O} (mPa s)	D_{N_2O,H_2O} ($\times 10^{-9}$ m^2 s^{-1})	PZ conc. (kmol m^{-3})	$\eta_{PZ\text{-}sol}$ (mPa s)	$D_{estimated}$ ($\times 10^{-9}$ m^2 s^{-1})
293.15	1.002	1.56	0.6	1.26	1.30
293.15	1.002	1.56	1.0	1.52	1.12
293.15	1.002	1.56	1.5	1.86	0.95
298.15	0.890	1.78	0.6	1.1	1.51
298.15	0.890	1.78	1.0	1.31	1.31
298.15	0.890	1.78	1.5	1.62	1.10

Table A.2
Comparison of Stokes–Einstein relation to experimental diffusivity data

T (K)	η_{H_2O} (mPa s)	D_{N_2O,H_2O} (10^{-9} m^2 s^{-1})	PZ conc. (kmol m^{-3})	$\eta_{PZ\text{-}sol}$[a] (mPa s)	$D_{estimated}$ (10^{-9} m^2 s^{-1})	$D_{experimental}$ (10^{-9} m^2 s^{-1})	Error (%)
303.15	0.798	2.03	0.23	0.887	1.87	1.91	−2.2
303.15	0.798	2.03	0.46	0.939	1.79	1.85	−3.5
303.15	0.798	2.03	0.69	1.004	1.69	1.77	−4.4
303.15	0.798	2.03	0.92	1.096	1.58	1.73	−8.8

[a]Taken from Sun et al. (2005).

by Versteeg and Van Swaaij (1988b):

$$D_{N_2O} = 5.07 \times 10^{-6} \exp\left(\frac{-2371}{T}\right). \tag{A.2}$$

Details and results of the calculation are listed in Table A.1.

The performance of this rather simple estimation method was tested with the experimental diffusivity data at 30 °C reported by Sun et al. (2005), at a concentration range from 0.23 to 0.92 kmol m^{-3}. A comparison between the experimental results and the values estimated by the modified Stokes–Einstein equation is given in Table A.2.

Although the modified Stokes–Einstein equation in its current form gives a fair prediction of the experimentally determined diffusion coefficients (the deviation is $< 10\%$), it should be noted that the prediction capability seems to deteriorate with increasing piperazine concentration (and hence solution viscosity).

Appendix B. Implementing reversibility in the calculation of the infinite enhancement factor

As already pointed out in Section 3, the reversibility of the reaction between CO_2 and piperazine has not been taken into account in the determination of the rate constant, since for the present experiments this reversibility does not influence the infinite enhancement factor or the calculated enhancement factor (by using Eq. (13)) substantially. In literature, some studies can be found which offer approximate solutions which are corrected for the reversibility of a reaction system. One of the methods to include reversibility in the expression for the infinite enhancement factor is provided by Secor and Beutler (1967).

Secor and Beutler (1967) derived an equation for the infinite enhancement factor which incorporates the reversibility of a reaction. The following reaction takes place:

$$\nu_A A + \nu_B B \rightleftarrows \nu_C C + \nu_D D. \tag{B.1}$$

The infinite enhancement factor (including reversibility) is defined as follows:

$$E_{A,\infty} = 1 + \frac{\nu_A D_C}{\nu_C D_A} \frac{([C]_i - [C]_L)}{(m[A]_G - [A]_L)}. \tag{B.2}$$

The concentration of C at the interface, C_i, is to be calculated using the following:

$$[B]_i = [B]_L + \frac{\nu_B D_C}{\nu_C D_B}([C]_L - [C]_i), \tag{B.3}$$

$$[D]_i = [D]_L - \frac{\nu_D D_C}{\nu_C D_D}([C]_L - [C]_i), \tag{B.4}$$

$$K = \frac{[C]_i^{\nu_C}[D]_i^{\nu_D}}{(m_A[A]_G)^{\nu_A}[B]_i^{\nu_B}}. \tag{B.5}$$

It is, however, not possible to directly compare the infinite enhancement calculated with Eq. (B.2) to the infinite enhancement used in this work (Eq. (10)), since the latter is based on the penetration theory, whereas Eq. (B.2) stems from the film theory. To comply with the penetration theory also, Eq. (B.2) was adapted similar to the method described by Hogendoorn et al. (1997). The reversible infinite enhancement factor is then given by

$$E_{A,\infty} = 1 + \left(\frac{D_C}{D_A}\right)^{0.5} \frac{\nu_A([C]_i - [C]_L)}{\nu_C(m[A]_G - [A]_L)}. \tag{B.6}$$

The overall reaction to be checked for the influence of reversibility is the following reaction between piperazine and

Table B.1
Conditions and properties of the calculation example for the reversible infinite enhancement factor

Property			Source
Temperature	298.15	K	Table 7
Initial piperazine concentration	600	$mol\,m^{-3}$	Table 7
CO_2 partial pressure	5.50	mbar	Table 7
Equilibrium constant	$8.0 \cdot 10^4$	m^{-1}	Table 2
Distribution coefficient	0.802	(–)	Table 6
Diffusion coefficient of CO_2	1.51×10^{-9}	$m^2\,s^{-1}$	Appendix A
Diffusion coefficient of PZ	0.90×10^{-9}	$m^2\,s^{-1}$	Eq. (19)

Table B.2
Interfacial concentrations calculated according to Eqs. (B.3)–(B.5)

$[PZ]_i$	68.6	$mol\,m^{-3}$
$[CO_2]_i$	0.18	$mol\,m^{-3}$
$[PZCOO^-]_i$	265.7	$mol\,m^{-3}$
$[PZH^+]_i$	265.7	$mol\,m^{-3}$

Table B.3
Calculation results for the infinite enhancement factor

Type	Equation no.	Value
Irreversible	(10)	1256
Reversible	(B.6)	1164

carbon dioxide:

$$CO_2 + 2PZ \rightleftarrows PZCOO^- + PZH^+. \quad (B.7)$$

The following assumptions have been made in the calculation of the enhancement factors according to Eq. (B.6):

- Diffusion coefficient of all piperazine species is equal.
- The system behaves ideally.
- No other reactions take place besides reaction (1) between piperazine and CO_2 to form carbamated and protonated piperazine.

The conditions applying to the example to be studied are listed in Table B.1.

Eqs. (B.3)–(B.5) can be used to calculate the corresponding concentrations at the gas–liquid interface necessary for the reversible infinite enhancement factor (Eq. (B.6)). Results are listed in Table B.2.

Now, both the infinite enhancement factors can be calculated and the results are shown in Table B.3.

The results in this calculation example show that the difference between the irreversible and reversible infinite enhancement factors is about 10% in the case of the kinetic rate experiments in $600\,mol\,m^{-3}$ at 25 °C. Similarly, also the reversible infinite enhancement factors have been calculated for the other kinetic data series, and the resulting values have been listed in Table 9 in Section 5.

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